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# EUROPEAN SEARCH REPORT

0244253

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 87303900.2
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
A	EP - A1 - O 146 284 (SONY CORPORATION) * Claims * --	1,9	C 23 C 14/08 C 23 C 16/40 B 32 B 15/04/ C 22 C 14/00
A	DD - A1 - 226 018 (FORSCHUNGS-INSTITUT MANFRED VON ARDENNE) * Claims * --	1,9	F 01 L 3/02 F 16 C 9/04
A	PATENT ABSTRACTS OF JAPAN, unexamined applications, C field, vol. 9, no. 271, October 29, 1985 THE PATENT OFFICE JAPANESE GOVERNMENT page 136 C 311 * Kokai-no. 60-121 276 (SONY K.K.) * -----	1,9	TECHNICAL FIELDS SEARCHED (Int. Cl. 4)  C 23 C B 32 B C 22 C F 01 L F 16 C F 16 K
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 20-07-1987	Examiner SLAMA
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

FIG.7

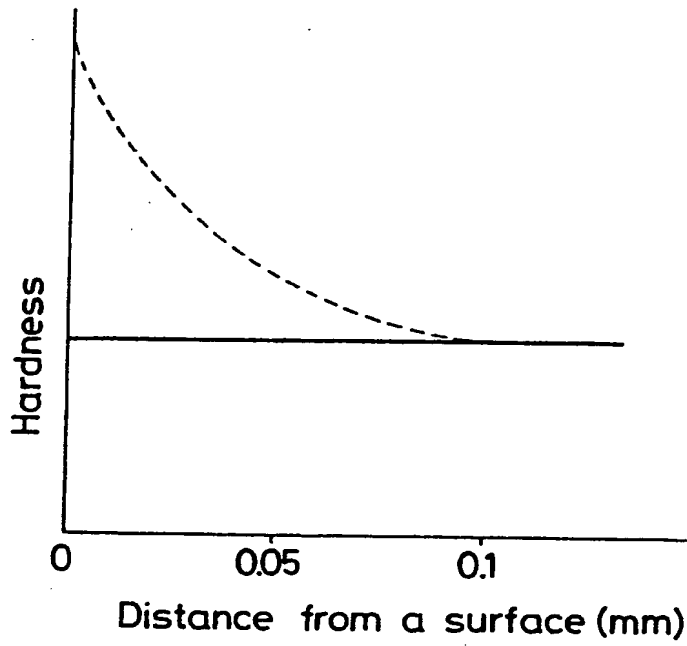


FIG.9

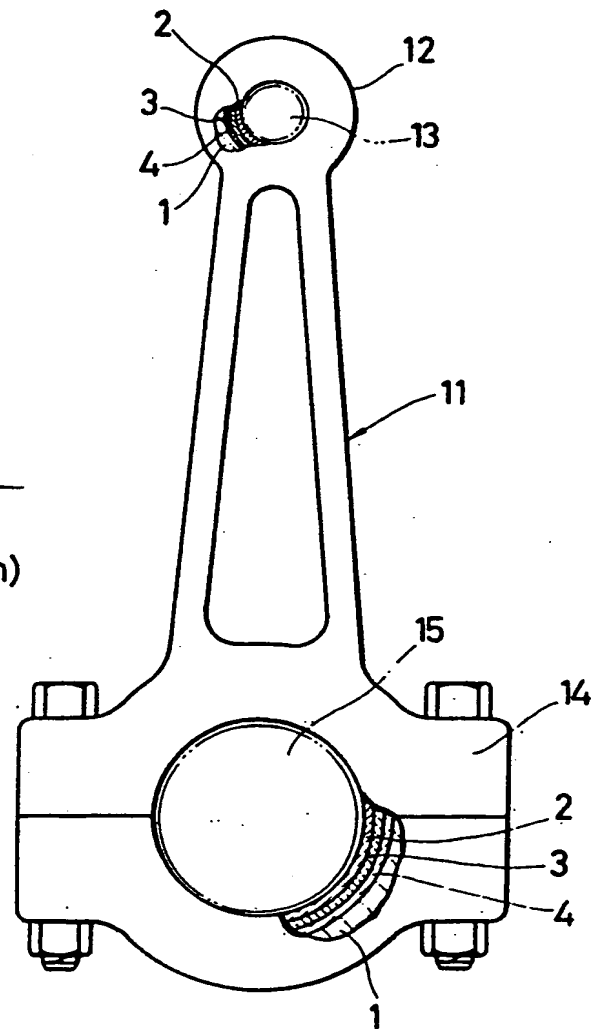
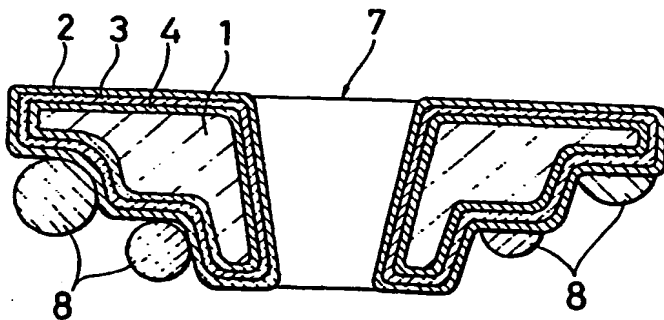


FIG.8



024425:

FIG.3

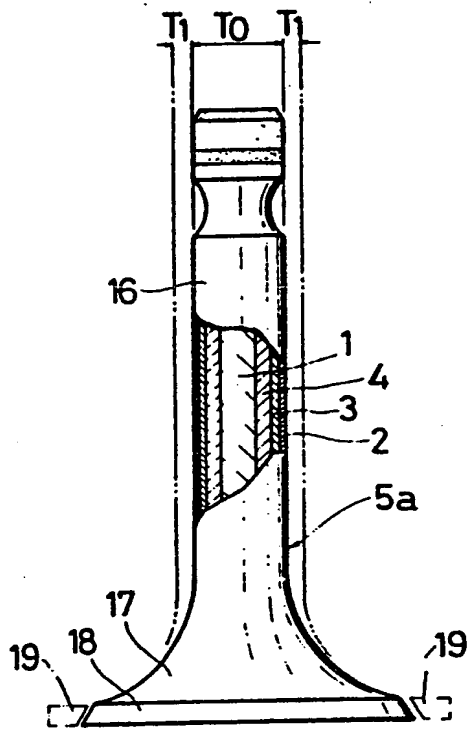


FIG.4

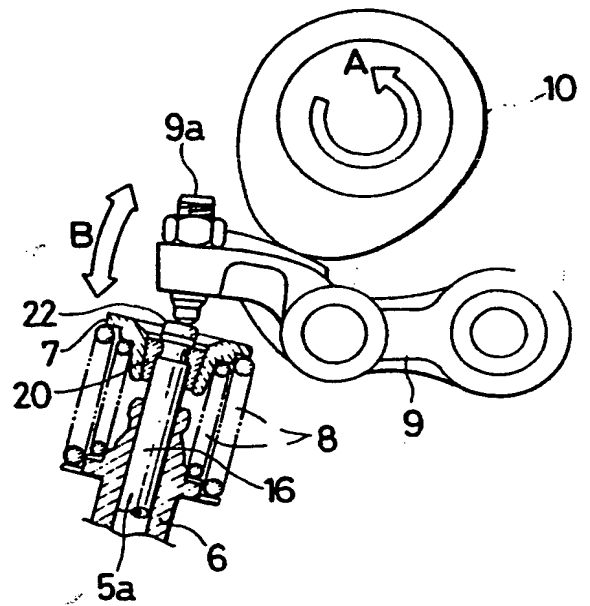


FIG.5

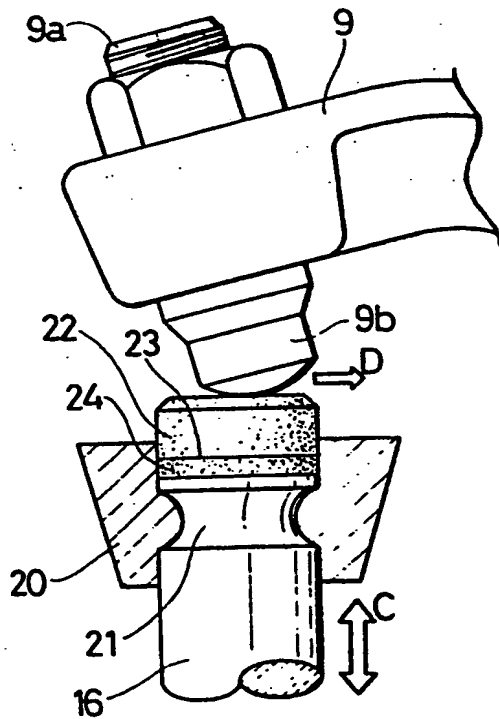


FIG.6

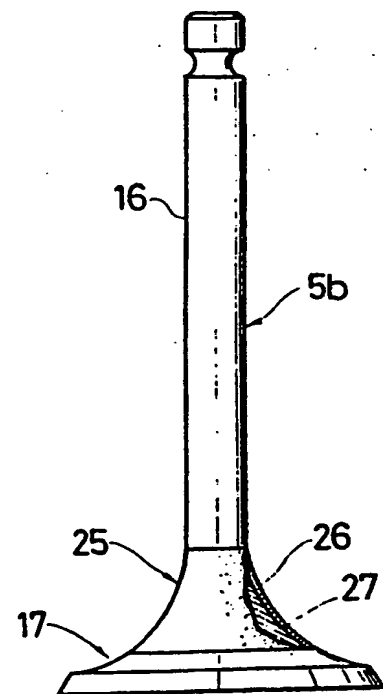


FIG.1A

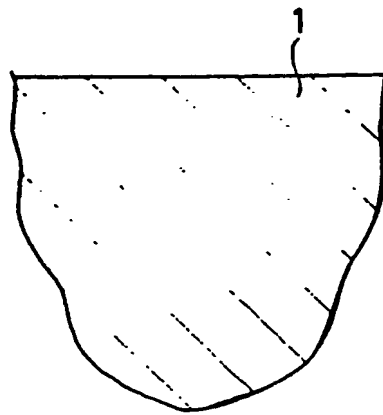


FIG.1B

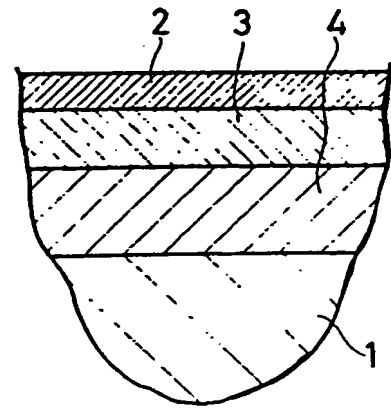
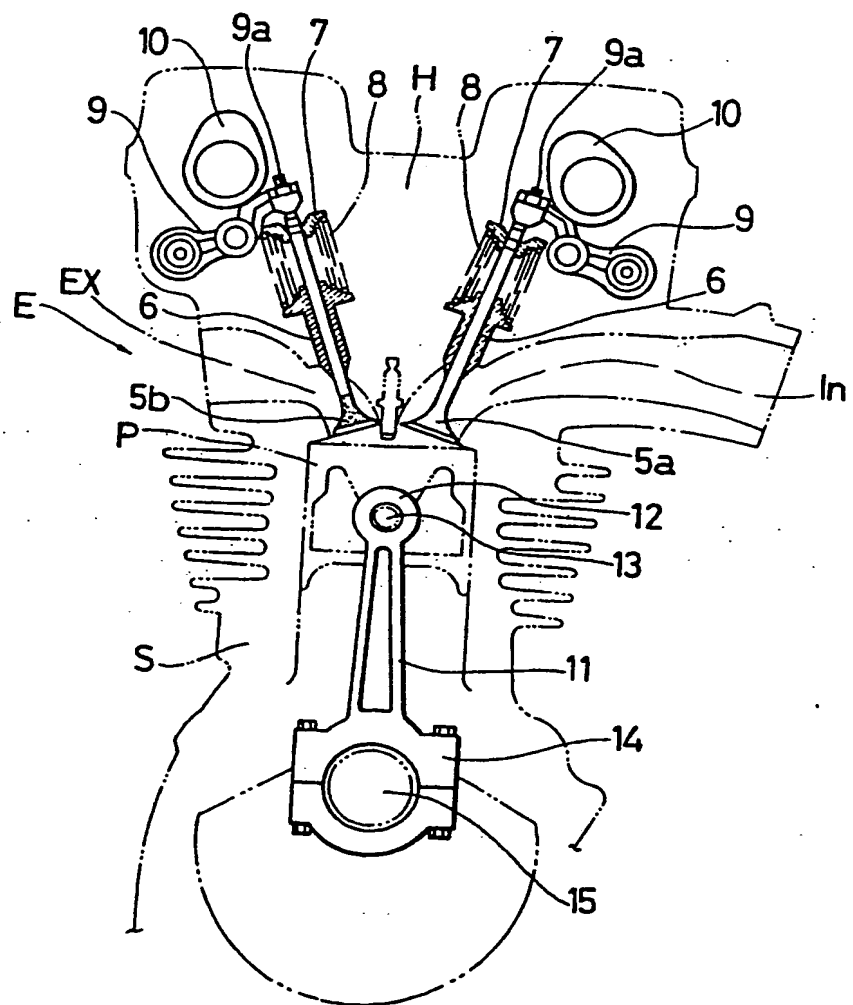


FIG.2



10. A process as claimed in claim 9 wherein the article is first formed by a method comprising stamping out the required shape of article from titanium metal or a titanium alloy.

5

11. A process as claimed in either of claims 9 and 10 wherein the temperature used for the heat treatment is between 500°C and 800°C.

one end of the valve spring 8 and said cotter 20 being adapted to surround the interface 23 between said disc-shaped layer of reinforcing material 22 and said heat-affected disc-shaped layer 24.

5

5. An article as claimed in claim 4 wherein said heat affected disc-shaped layer 24 does not comprise said cotter groove 21 or any part thereof.

10 6. An article as claimed in any one of claims 3 to 5 being an exhaust valve having an oxide prevention layer forming the surface of the valve poppet means 17 and/or the valve stem 16 at the area of contact thereof.

15

7. An article as claimed in claim 1 being a valve retainer adapted for use in the valve actuating mechanism of an engine.

20 8. An article as claimed in claim 1 being a connecting rod adapted to connect the piston and the crankshaft of an engine.

25 9. A process for treating the surface of a titanium or titanium alloy article which comprises heat treating the titanium or titanium alloy article in an oxygen-containing atmosphere at a temperature below 800°C for a period of time whereby a surface treatment oxide covering comprising a hard titanium  
30 oxide outer layer, a heat-modified titanium or titanium alloy inner layer one surface of which contacts the unchanged titanium metal or titanium alloy, and a chemically modified titanium or titanium  
35 oxide outer layer and the heat-modified titanium or titanium alloy inner layer is formed on at least part of the surface of the said article.

CLAIMS:

1. A titanium or titanium alloy article at least part of the surface of which comprises a surface treatment oxide covering produced by direct oxidation of the titanium or titanium alloy of the surface,  
5 the said surface treatment oxide covering comprising a hard titanium oxide outer layer, a heat-modified titanium or titanium alloy inner layer one surface of which contacts the unchanged titanium metal or titanium alloy, and a chemically modified titanium  
10 or titanium alloy intermediate layer between the hard titanium oxide outer layer and the heat-modified titanium or titanium alloy inner layer.
2. An article as claimed in claim 1 wherein  
15 at least those surfaces of said article that are adapted to contact or to slidably interact with other moving parts comprise said surface treatment oxide covering.
- 20 3. An article as claimed in either of claims 1 and 2 being a poppet valve comprising a valve poppet means 17 and a valve stem 16 and adapted for use as an intake or exhaust valve in an engine wherein the surface of at least said valve stem 16 comprises  
25 said surface treatment oxide covering.
4. An article as claimed in claim 3 wherein said valve stem 16 has a circumferentially disposed cotter groove 21 at the tip end thereof and is  
30 provided with a disc-shaped layer of reinforcing material 22 with a heat-modified titanium or titanium alloy disc-shaped layer 24 being situated between said disc-shaped layer of reinforcing material 22 and the tip of said valve stem 16, said cotter  
35 groove 21 engaging with a cotter 20, said cotter 20 being sheathed by a valve retainer 7 which supports

bush and the prior art treatment process therefor. Since the big end of the connecting rod at the point at which it contacts the crankshaft 15, is also covered by a surface treatment oxide covering, 5 no treatment such as molybdenum injection welding is needed.

It is possible to form the surface treatment oxide covering on the whole surface, such as the present embodiment, or only on part of the surface 10 by masking the remainder of the surface from oxygen. A partial oxide surface treatment covering may be formed on other articles as required. In the preferred embodiment described hereinbefore, use is made of the hard titanium oxide outer layer 15 as the surface treatment layer. Thus there is no need to remove this layer as required in the prior art since it is fully utilised. Thus it can save material, and can improve the compactness and the lightness of the product. When using articles 20 in a reciprocating mechanism such as a valve actuating system, it is beneficial to improve the sliding-interaction to improve the performance. The use of an atmospheric oven in the production of articles makes it possible to produce such heat treated articles cheaply.

It should be understood that the present invention is not limited to the above-mentioned embodiments. The invention may be adapted to various types of articles, for example crankshafts or rocker 30 arms in respect of engine parts.



shape of the article after heat treatment. However the surface of a valve retainer comprising a surface treatment oxide covering according to the present invention is very smooth compared with the surface of a valve retainer which has undergone nitrogen treatment and it also has high surface hardness, thus giving good wear resistance.

An article prepared by the process of the present invention experiences little reciprocal surface wear between the valve retainer and the end of the valve spring 8. Thus even if a rough edge is produced by the method of manufacture nevertheless it may be durable enough and there is no need for additional special treatment. Since the heat treatment process requires a comparatively low temperature (below 800°C) any heat deformities may be small enough that there will be no need to remove them.

Fig 9 shows the connecting rod 11 in detail. The connecting rod 11 has a hard titanium oxide outer layer 2, a chemically modified titanium or titanium alloy intermediate layer 3 and a heat-modified titanium or titanium alloy inner layer 4 produced by the process of the invention. The surface treatment layer is provided on the point where the small end portion 12 thereof contacts the piston 13. As the small end portion of the connecting rod is connected to the piston pin, a bush made of copper is inserted in order to maintain wear resistance and protect against the reciprocating rod. The reciprocating rod, which is inserted into the crankshaft, carries a surface treatment layer formed by the molybdenum injection welding in order to maintain the wear resistance. Since the connecting rod 11 comprises a surface treatment oxide covering on the portion of the small end thereof which contacts the piston pin 13, there should be no need for the copper bush. i.e. there is no need for the insertion process for the copper

of the same hardness on going from the surface to the inside portion thereof; that is to say, it is hardly oxidized.

Formation of the oxide prevention layer 26 on the joint portion should not adversely affect the titanium layer 27 on the joint portion 25. Therefore, it is possible to avoid any adverse effects caused by the oxide layer such as variation of strength along an exhaust valve that is used under such conditions of high temperature and an oxygen-containing atmosphere. The oxide prevention layer can also be adapted to the intake valve 5a.

Fig 8 shows the valve retainer 7 on an enlarged scale. The valve retainer 7 is manufactured having a step portion which can be used to support the end portion of the valve spring. A surface treatment oxide covering comprising a hard titanium oxide outer layer 2, a chemically modified titanium or titanium alloy intermediate layer 3 and a heat-modified titanium or titanium alloy inner layer 4 is formed on the whole surface thereof by means of heat treatment according to the present invention. In comparison, in the prior art process the valve retainer undergoes nitrogen treatment on the whole surface thereof under high temperature conditions, for example 800-1000°C, resulting in the formation of a comparatively rough surface (the nitrogen treatment layer). The rough surface wears the end of the valve spring, forming a sharp edge which reciprocally wears the area of the valve retainer in contact therewith.

In order to avoid such reciprocal wear of surfaces as much as possible, the valve spring end should be moulded so that it is difficult to form a hard edge. Since nitrogen treatment requires high temperatures, over 800°C, stress produced by heat deformation must be relieved by a skilful and complicated process in order to maintain the

of the titanium layer 27. Finally the oxide prevention layer 26 covers the strong joint portion 25 such that said joint portion 25 is not contacted directly by the exhaust gas. By ensuring that the oxide prevention layer 26 will cover the titanium layer 27 on the joint portion 25, the surface of the titanium layer 27 can be protected from oxidation. Tin can conveniently be used as the metal for the oxide prevention layer 26. The method for manufacturing the oxide prevention layer 26 is not limited to injection welding. Of greatest importance is that the oxide prevention layer be made strong integrally with the titanium metal by means of the diffusion joint. When the surface treatment oxide covering covers the valve stem 16, the oxide prevention layer 26 may be prepared using a prior art process. If the oxide prevention layer is to be added after the surface treatment oxide covering is already present, the process for preparing the oxide prevention layer should be directed to the concerned area. The joint portion 25 on which the oxide prevention layer 26 is formed should be curved to the least extent possible at the connecting point between the poppet means 17 and the valve stem 16 where the stress concentration will be a maximum.

Fig 7 shows the oxide resistance characteristics of an oxide prevention layer 26. This graph shows the variation of hardness caused by oxidation at various distances from the surface of each joint portion for a titanium metal valve comprising a Ti-6Al-4V alloy without the oxide prevention layer. Where the titanium metal is oxidized, the oxide layer increases the surface hardness. The dotted line represents conventional behaviour. Thus, it can be seen that the hardness rapidly increases at the titanium surface.

The hardness characteristic of a preferred embodiment of the present invention is shown as a continuous line in Fig 7. This shows the maintenance

tangential to the valve stem 16 (indicated by arrow D) which tends to break the connecting portion 23. However, since the connecting portion 23 is surrounded by the cotter 20, the impact force imparted by the rocker arm 9 is absorbed by the cotter 20. The impact force acting on the connecting portion 23 will be lowered and so the connecting portion 23 may be strong enough to resist the tendency to break. Such a connecting portion 23 is stronger than those described in the prior art which are not surrounded by the cotter with a consequent improvement in endurance characteristics. The same construction can also be adapted to the exhaust valve 5b. Materials for the reinforcing layer 22 can be selected as desired dependent upon the usage and so on.

An exhaust valve 5b manufactured in accordance with the process of the present invention will be described with reference to Figs 6 and 7. Since the exhaust valve 5b and especially the poppet means of said exhaust valve 5b always operate at high temperature, the titanium metal surface will be easily oxidized. Since the exhaust valve is usually subjected to high stress, it is desirable to prevent such oxidation. Therefore on the exhaust valve 5b there is provided an oxide prevention layer 26 on the surface of the joint at the connection between the poppet means 17 and the valve stem 16. The exhaust valve 5b is made of a titanium alloy composed of Ti-6Al-4V. Another alloy such as for example Ti-6Al-2Sn-4Zr-2Mo can also conveniently be used. The oxide prevention layer 26 may be made by a prior art method in which an aluminium compound is injected into the surface of the titanium metal valve. The injection initially produces an aluminium layer on the oxidized joint portion 25 and then a chemical combined layer is formed by a diffusion reaction between the aluminium layer and the surface

20 in the direction of the rocker arm 9. The reinforcing layer 22 is conveniently made of material of sufficient strength to be resistant to the impact stress and wear caused by the rocker arm 9. A suitable reinforcing layer material is an iron alloy such as JIS SCM440 (chrome-molybdenum steel) which may be attached to the valve stem 16 by friction welding.

After applying the process, the end portion of the valve stem 16 may be hardened to  $> 50^{\circ}$  on the Rockwell Scale of Hardness by heat treatment, this being equal to the hardness of a common iron valve. Whilst connecting the reinforcing layer disc 22 to the valve stem 16 the heat-modified titanium or titanium alloy inner layer 24 is formed in the titanium valve stem 16 adjacent the connecting portion 23 where it is surrounded by the valve cotter 20 and does not extend to the cotter groove 21. Thus the cotter groove 21 at the stress centre can be protected from various weaknesses generated by the connecting portion 23 and the heat-modified titanium or titanium alloy inner layer 24. It is desirable to position both the connecting portion 23 and the heat-modified titanium or titanium alloy inner layer 24 within the zone surrounded by the cotter 20 above the cotter groove 21 in order to maintain reasonable strength.

The tip end 9b of the tappet adjust screw 9a provided in the forward portion of the rocker arm 9 is adapted to contact the reinforcing layer 22. As shown in figs 4 and 5, when the cam 10 rotates in the direction indicated by arrow A in contact with the rocker arm 9, the forward end portion of the rocker arm 9 is swung in the direction indicated by arrow B and then the valve stem 16 is moved in the up and down directions as indicated by arrow C. Under this operation the tip end portion 9b of the tappet adjust screw will subject the reinforcing layer 22 to an impact force in a direction

substantially the same as that of an intake valve according to the prior art having an injection layer. Consequently it is possible to narrow the outer diameter  $T_1$  of the intake valve 5a to an extent equal to that given by the prior art injection layer. The inside diameter  $T_0$  is just identical with that of a prior art valve comprising base metal in order to produce a valve of similar strength. The presence of the hard titanium oxide outer layer 2 in the surface generally has a negligible effect on the durability for a given product strength. If it is necessary to improve the durability then this can be easily achieved by a small increase of the outside diameter or by a small decrease in the thickness of the hard titanium oxide outer layer 2 achieved by altering the heat treatment conditions. Since a continuous surface treatment oxide covering is formed on the seat portion 18, the wear resistance is sufficient and it is not necessary to use an expensive beryllium-copper alloy treatment.

It is also possible to form a surface treatment oxide covering on the surface of an exhaust valve 5b. The detailed construction of the valve will now be described with reference to Figs 4 to 7.

Fig 4 shows the valve stem 16 of the intake valve 5a on an enlarged scale. In order to mount the valve retainer 7 on the valve stem 16, the cotter 20 is mounted into the cotter groove 21 which is formed at the end portion of the valve stem 16 which should be the stress centre of the valve stem 16. There is provided a reinforcing layer 22 at the end portion of the valve stem 16 in order to improve wear resistance. The connecting portion 23 between the reinforcing layer 22 and the valve stem 16 is surrounded by the cotter 20. However, the upper end of the reinforcing layer 22 projects from the upper surface of the cotter

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hereinabove have surface treatment oxide coverings made by the process of the invention. These parts will be described in detail as follows:

Fig 3 illustrates on an enlarged scale the  
5 intake valve 5a which is made of the titanium metal. The intake valve 5a has a valve stem 16 and a valve poppet means 17, and is completely contacted by the valve seat 19 provided in the intake port. The intake valve 5a is manufactured by the above  
10 mentioned heat treatment process according to the invention and its whole surface comprises a hard titanium oxide outer layer 2, a chemically modified titanium or titanium alloy intermediate layer 3 and a heat-modified titanium or titanium alloy  
15 inner layer 4. The hardness of the intake valve surface is either equal to or better than that of a valve produced by the prior art process, that is, the surface registers at least 500° on the Vickers Scale of Hardness. Therefore, further  
20 surface treatment of the valve stem 16 which can be used in sliding contact with the valve retainer 6 is not required. According to the prior art it is necessary to form a special surface treatment layer by molybdenum injection welding in order  
25 to maintain the inter-slidability of these parts. Such a prior art process possesses disadvantages in that the parts will be of larger diameter and will be heavier in weight. Furthermore, when using molybdenum injection welding, a pre-treatment comprising  
30 mechanical processes such as cutting, sandblasting and an after-treatment comprising a finishing process such as surface planing are required.

In addition, the wear resistance of the valve poppet means should be improved without the need  
35 for surface treatment using an expensive beryllium-copper alloy on the seating portion of the valve seat. The inside diameter  $T_o$  of an intake valve 5a having a surface treatment oxide covering is

is desirably used. It is preferable to maintain the temperature above a minimum of 500°C. While it is possible to carry out the heat treatment at a lower temperature using a long time period, this may decrease efficiency. Consequently, it is preferable to use a heat treatment temperature of 500-800°C.

The treatment time can vary from several minutes to a few hours depending on the heat treatment temperature chosen. A preferred treatment time is 3-5 hours.

Fig 2 is an outside view of a motorcycle engine which comprises components produced according to the present invention. The engine E consists of a cylinder S and a cylinder head H, and a piston P is slidably mounted in the cylinder S. An intake port In, an exhaust port Ex and a valve mechanism having an intake valve 5a and an exhaust valve 5b, which are manufactured from titanium metal, are provided. The following is a description of the intake valve mechanism (the exhaust valve mechanism is identical with the intake valve mechanism).

The intake valve 5a is slidably mounted in the valve guide 6. The valve retainer 7 is fixed at the end portion of the intake valve 5a and the valve spring 8 is disposed between the valve retainer 7 and the valve guide 6. The end tip of the intake valve 5a is in contact with the tappet screw 9a which is screwed on to the forward end portion of the rocker arm 9, the rocker arm 9 being pivotally movable in both the upward and downward directions by means of a cam 10 formed on the cam shaft so that the intake valve 5a is lifted at the predetermined angle. A connecting rod 11 made of titanium metal is connected to the piston P. The connecting rod 11 is connected to the piston pin 13 at the small end thereof and connected to the crankshaft 15 at the big end thereof. The intake valve 5a, the valve retainer 7 and the connecting rod 11 as mentioned



process on the titanium metal surface after stamping it to the required form of article. The outer surface is the base material 1 of the titanium metal itself. At first the product is put into  
5 an oven such as an atmospheric oven with an oxygen-containing atmosphere and is heated at a temperature below 800°C for a period of several minutes to a few hours. This results in the formation of the hard titanium oxide outer layer 2, a chemically  
10 modified titanium or titanium alloy intermediate layer 3 and a heat-modified titanium or titanium alloy inner layer 4 on the base material 1 in this order moving from the outer surface of the article. Thus, the "surface treatment oxide covering" comprises  
15 a hard titanium oxide outer layer 2, a chemically modified titanium or titanium alloy intermediate layer 3 and a heat modified titanium or titanium alloy inner layer 4.

Since the hard titanium oxide outer layer  
20 2 is a layer of titanium oxide, the surface of the article is very hard, registering over 500° on the Vicker Scale of Hardness. Such a surface is substantially as hard as a surface produced by the prior art methods. Furthermore, the surface  
25 after heat treatment according to the invention does not require any additional finishing process after the heat treatment. The treated surface is acceptable as the outer surface of the product.

Various types of chemical compounds are formed  
30 in the chemically modified titanium or titanium alloy intermediate layer 3 by the combination of titanium with oxygen, nitrogen and carbon dioxide in the atmospheric air within the oven. The thickness of the surface treatment oxide covering can be  
35 reasonably controlled depending on the temperature and the time of the treatment. If the temperature is too high, however, stress would be generated in the product. Thus a temperature of below 800°C

resistance. Accordingly there is no need for further surface treatment such as molybdenum injection welding and nitrogen treatment. Thus the process of the present invention can improve efficiency  
5 by removing the need for various kinds of pre-treatment and after treatment steps such as finishing and stress-relieving treatments.

In the process according to the present invention, an atmospheric oven (i.e. an oven in which articles  
10 are heated in air) may be used to effect heat treatment in the temperature range 500-800°C. Thus the surface treatment may be effected cheaply and at high speed using an atmospheric oven.

Preferred embodiments of the invention will  
15 now be illustrated with reference to the accompanying drawings in which:

Figs 1A and 1B are respectively partial cross-sectional views through the surface of an article before and after carrying out the process according  
20 to the present invention, the layer thicknesses being shown on an enlarged scale.

Fig 2 is a cross-sectional view through a motorcycle engine comprising articles made in accordance with the present invention.

25 Fig 3 is an outside view, partly in section, of a valve.

Figs 4 and 5 are cross-sectional views showing main portions of an intake valve.

Fig 6 is an outside view of the main portion  
30 of an exhaust valve.

Fig 7 is a graph showing surface hardness characteristics.

Fig 8 is an enlarged cross-sectional view of a valve retainer.

35 Fig 9 is an illustration, partly in section, of a connecting rod.

Fig 1A shows a cross-section through the manufactured surface produced by applying a finishing

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other moving parts then it is preferable that those surfaces comprise a surface treatment oxide covering.

Articles manufactured according to the invention show a number of advantages. The hard titanium oxide outer layer forming the outer surface of the surface treatment oxide covering may form the outer surface of the article. Thus, since the titanium oxide forms a hard outer surface to the titanium articles, it is not necessary to provide another hard surface. Furthermore, the surface treatment oxide layer itself may strengthen the construction of the articles; such a strengthening effect is not produced by the surface treatment disclosed in the prior art. Further advantages are the lightness and compactness of the articles. In contrast with the prior art in which the hard titanium oxide outer layer must be removed from the surface of the article, with the articles of the present invention the hard titanium oxide outer layer can be used effectively, thus making the use of materials more efficient.

Titanium articles for use as engine components such as valves, valve retainers adapted for use in the valve actuating mechanism of an engine, connecting rods adapted to connect the piston and the crankshaft of an engine and so on are examples of articles which are usefully treated according to the present invention. The hard titanium oxide layer on the outer surface, can improve the sliding action of such articles in slidable contact with other engine parts and it can also improve the weight of the engine reciprocating mass.

As the temperature used in the process according to the invention must be below 800°C during the process, undesired stress will not be produced in the treated articles according to the invention.

The hard titanium oxide outer layer can have the same or greater hardness than the surfaces obtained by treatments according to the prior art and thus has good wear resistance and good seizure

and titanium alloy articles which may be produced by the process.

According to one feature of the present invention, there is thus provided a titanium or titanium alloy article at least part of the surface of which comprises  
5 a surface treatment oxide covering produced by direct oxidation of the titanium or titanium alloy of the surface, the said surface treatment oxide covering comprising a hard titanium oxide outer layer, a heat-modified titanium or titanium alloy  
10 inner layer one surface of which contacts the unchanged titanium metal or titanium alloy, and a chemically modified titanium or titanium alloy intermediate layer between the hard titanium oxide outer layer and the heat-modified titanium or titanium alloy  
15 inner layer.

In the present context the "hard titanium oxide layer" is defined as a titanium oxide layer which registers at least 500° on the Vicker Scale of Hardness.

20 According to a further feature of the present invention, there is provided a process for treating the surface of a titanium or titanium alloy article which comprises heat treating the titanium or titanium alloy article in an oxygen-containing atmosphere  
25 at a temperature below 800°C for a period of time, preferably from 1 minute to less than 10 hours, whereby a surface treatment oxide covering comprising a hard titanium oxide outer layer, a heat-modified titanium or titanium alloy inner layer one surface  
30 of which contacts the unchanged titanium metal or titanium alloy, and a chemically modified titanium or titanium alloy intermediate layer between the hard titanium oxide outer layer and the heat-modified titanium or titanium alloy inner layer is formed  
35 on at least part of the surface of the said article. The heat treatment is preferably carried out at a temperature in the range of from 500 to 800°C.

When such articles comprise surfaces that are adapted to contact or slidably engage with

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Surface treatment of titanium articles

The present invention relates to the surface treatment of titanium articles, especially titanium metal or titanium alloy articles which may be adapted for use in engines for motorcycles or other vehicles.

5        Engine parts for motorcycles and other motor vehicles may usefully be manufactured from titanium or titanium alloys. The advantages of using titanium metal are that titanium products exhibit the properties of lightness, great hardness, high heat resistance,  
10        etc.; therefore there has been a tendency for titanium-based parts to be used in high performance motor vehicles such as vehicles used for motor racing or motorcycle racing. However, when using titanium metal-based engine parts, wear resistance and seizure  
15        resistance must be considered and furthermore removal of the oxide layer on the titanium metal is necessary in order to improve durability.

      In the art the process for producing such articles generally involves stamp forging the titanium  
20        metal, removing the hard titanium oxide outer layer on the metal surface and then subjecting the surface to molybdenum injection welding or to nitrogen treatment. Furthermore, heat treatment should be performed in an argon atmosphere or in vacuo.  
25        Valves, valve retainers and connecting rods are examples of articles which may be manufactured in such a manner from titanium.

      It is one object of the present invention to provide a new process for the treatment of titanium  
30        and titanium alloy articles whereby such articles having desired properties can be produced without the necessity for removing hard titanium oxide from the metal surface. It is a further object of the present invention to provide novel titanium

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

(11) Publication number:

**0 244 253**  
**A1**

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: 87303900.2

(22) Date of filing: 30.04.87

(51) Int. Cl.<sup>3</sup>: **C 23 C 14/08**

**C 23 C 16/40, B 32 B 15/04**  
**//C22C14/00, F01L3/02, F16C9/04**

(30) Priority: 30.04.86 JP 100530/86

(43) Date of publication of application:  
04.11.87 Bulletin 87/45

(84) Designated Contracting States:  
DE FR GB

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(54) Surface treatment of titanium articles.

(57) There is disclosed a titanium or titanium alloy article at least part of the surface of which comprises a surface treatment oxide covering produced by direct oxidation of the titanium or titanium alloy of the surface, the said surface treatment oxide covering comprising a hard titanium oxide outer layer as a wear surface.

This process is especially suitable for treating those surfaces of engine parts, for example valves, valve retainers and connecting rods, that are either in contact or in sliding contact with other engine parts.